



Case OR-7289  
Appln. No. 10/751,144

THE UNITED STATES PATENT AND TRADEMARK OFFICE

**SAMUEL A. SANGOKOYA, ET AL.**

**APPN. NO.: 10/751,144**

**FILED: DECEMBER 31, 2003**

**HALOALUMINOXANE  
COMPOSITIONS, THEIR  
PREPARATION, AND THEIR USE IN  
CATALYSIS**

**GROUP ART UNIT: 1713**

**EXAMINER: CAIXIA LU**

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

**DECLARATION UNDER 37 CFR § 1.132**

Samuel A. Sangokoya hereby declares as follows:

1. I am one of the Applicants in the above-entitled application.
2. I am a chemist employed by Albemarle Corporation, the assignee of the above-identified application by unrecorded assignment.
3. In 1983, I received the degree of Ph.D. in chemistry from the University of Maryland.
4. Since 1989 I have been continuously employed as a chemist by Albemarle Corporation and the predecessor thereof, Ethyl Corporation, at the research laboratory facilities in Baton Rouge, Louisiana.
5. The test work described herein is the same as that submitted as Exhibit B accompanying a Response filed in this case on May 1, 2006.
6. The test work described herein was conducted by me at the Albemarle Process Development Center in Baton Rouge, Louisiana. In this work, the preparation of Halogenated Aluminoxane-I and Halogenated Aluminoxane-II of Kioka et al. in Example 31 of U.S.3,063,726 was repeated. The ethylene polymerization of Halogenated Aluminoxanes-I and -II was studied and compared with that of methylaluminoxane (MAO) and other haloaluminoxanes.

7. The syntheses of the various aluminxanes is as follows:
  - Halogenated Aluminoxane I was prepared as described in Example 31 of Kioka et al., which used the procedure of Example 24 of Kioka et al. for preparing Aluminoxane I, from dimethylaluminum chloride (46 mL) and  $\text{Al}_2(\text{SO}_4)_3 \cdot 14 \text{H}_2\text{O}$  (37 g) in toluene (125 mL). Halogenated Aluminoxane II was prepared similarly, from trimethylaluminum (24.7 mL) and dimethylaluminum chloride (25.3 mL).
  - A chlorinated methylaluminoxane composition was obtained by treating a toluene solution of methylaluminoxane (MAO, 20 g, 103 mmol Al) with dimethylaluminum chloride (103 mmol Cl). The slightly cloudy MAO solution became clear. The mixture was heated at 70°C for one hour and then filtered. The ratio of chlorine to aluminum in the chlorinated MAO was about 50 mole %.
  - A chlorinated methylaluminoxane composition of the invention (Cl-MAO) was obtained by treating a toluene solution of MAO (20 g, 103 mmol Al) with dimethylaluminum chloride (10.3 mmol Cl). The clear solution was heated and filtered. The ratio of chlorine to aluminum in the Cl-MAO was about 5 mole %.
  - A fluorinated methylaluminoxane composition of the invention (F-MAO) was obtained in a manner similar to that of Example 4 of the Specification of the above-referenced case. The ratio of fluorine to aluminum in the F-MAO was 4 mole %.
  - Methylaluminoxane (MAO) manufactured by Albemarle was obtained from stock solutions and used as standard for comparison.
8. Homogeneous ethylene polymerization tests were carried out in a 2 L autoclave equipped with a magnetic stirrer and temperature and pressure monitors, using isohexane as solvent. The reaction temperature was maintained at 70°C, and the pressure was maintained at 140 psig respectively for 15 minutes during polymerization. Rac-1,2-bis[indenyl]-ethylene-zirconium dichloride ( $2.15 \times 10^{-6}$  mol) was used in all cases as the metallocene catalyst. The catalyst and the Cl-MAO solution were added simultaneously to the autoclave, through separate inlets, followed by the introduction of high pressure ethylene gas. The reaction with F-MAO was too hot and uncontrollable, requiring a reduction of both the Al and Zr values. A metallocene amount of  $1.08 \times 10^{-6}$  mole was used with the F-MAO. The results are summarized in the Table below.

TABLE

Activator	Molar ratio Al:Zr	Zr content	Activity (g PE)
MAO	400	2.15 $\mu$ mol	50.0
Halogenated Aluminoxane-I	400	2.15 $\mu$ mol	0.0
Halogenated Aluminoxane-II	400	2.15 $\mu$ mol	0.4
Cl-MAO (50 mole % Cl:Al)	400	2.15 $\mu$ mol	2.3
Cl-MAO (5 mole % Cl:Al)	400	2.15 $\mu$ mol	23.2
F-MAO (4 mole % F:Al)	400	1.08 $\mu$ mol	52.5

9. The  $^1\text{H}$  NMR spectra of four of the above halogenated aluminoxanes, portions of which spectra are provided herein, are shown below. The spectra are plotted on the same scale in the region 1 to  $-1.5$  ppm with respect to tetramethylsilane (TMS).

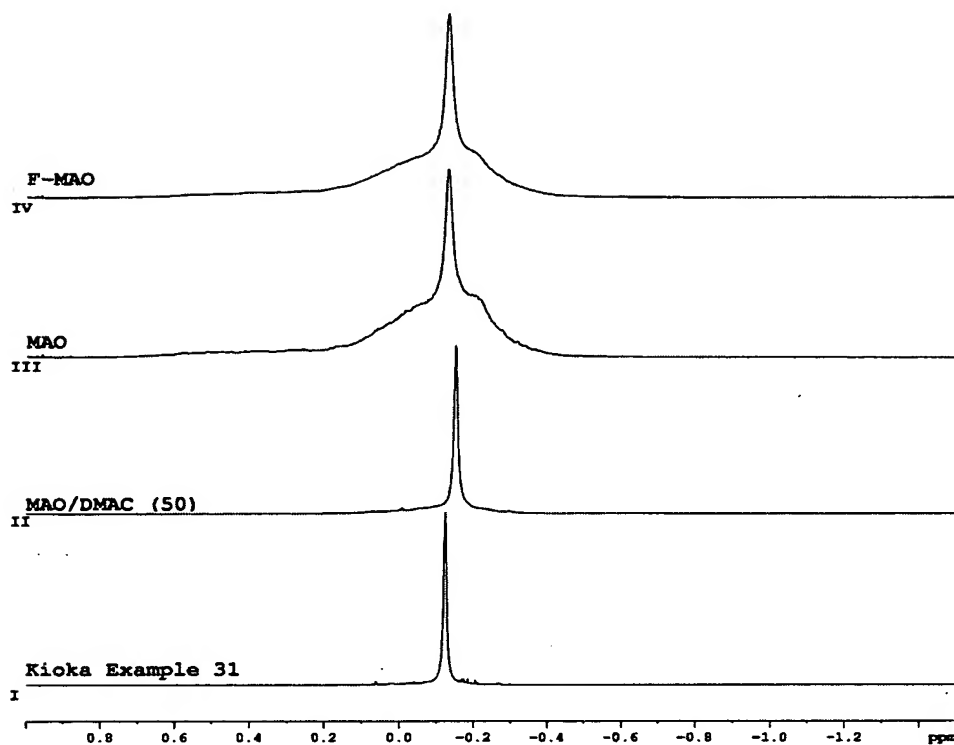
▪ Spectrum I (Kioka Example 31) is for Halogenated Aluminoxane I of Example 31 of Kioka et al., which halogenated aluminoxane was made by hydrolyzing dimethylaluminum chloride. There is no characteristic fingerprint of MAO (see Spectrum III) in Spectrum I.

▪ Spectrum II (MAO/DMAC (50)) is for the chlorinated methylaluminoxane obtained by treating methylaluminoxane with dimethylaluminum chloride, in which the ratio of chlorine to aluminum was about 50 mole %. The characteristic fingerprint of MAO has disappeared from the spectrum.

▪ Spectrum III (MAO) is for methylaluminoxane (MAO), and shows the broad band characteristic of MAO centered at about  $-0.1$  ppm.

▪ Spectrum IV (F-MAO) is for the fluorinated methylaluminoxane of the present invention in which the ratio of fluorine to aluminum was about 4 mole %. The characteristic fingerprint of MAO is present in this spectrum.

### Proton NMR Spectra of Haloaluminoxanes



10. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date: August 17, 2006

  
Samuel A. Sangokoya